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BOSTON UNIVERSITY
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Thesis

THE PREPARATION OF N-(NITROALKYL)-ANILINES

by

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TABLE OF CONTENTS

Introduction..1

Preparation of Azomethines.......... 4

Benzalaniline...4

α-Ethyl-β-Propylacrolein Anil...................................4

Benzalisopropylamine..5

Butyraldehyde Anil..6

Reactions of Azomethines with Nitroparaffins....................13

Reaction of Butyraldehyde Anil with Nitromethane................15

Reaction of Butyraldehyde Anil with Nitroethane.................18

Reaction of Benzalaniline with Nitroethane......................22

Reaction of Benzalaniline with Nitropropane.....................29

Reaction of Benzalaniline with Nitromethane.....................31

Reaction of α-Ethyl-β-Propylacrolein Anil with Nitromethane..38

Reaction of Benzalisopropylamine with Nitromethane..............41

Preparation of 2-Nitrobutene-1..................................43

Reactions of Aromatic Amines with 2-Nitrobutene-1...............49

N-2-Nitrobutylaniline...49

N-(2-Nitrobutyl)-p-Nitroaniline.................................51

N-(2-Nitrobutyl)-α-Naphthylamine..............................53

N-(2-Nitrobutyl)-p-Toluidine....................................54

N,N'-Di-(2-Nitrobutyl)-o-Phenylenediamine.......................55

Summary...57

Bibliography..60

INTRODUCTION

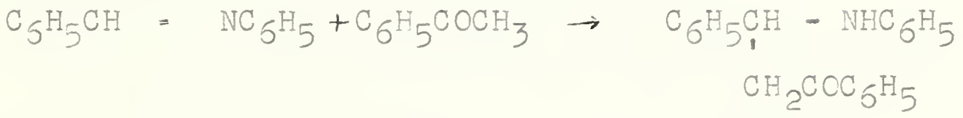
It is known that where there are at least two hydrogens on the alpha carbon to the nitro group of a nitroparaffin, one of these alpha hydrogens is sufficiently reactive to cause an aldol type of condensation of the nitroparaffin with such unsaturated groups as the carbonyl group. In the case of nitromethane, two or three of the alpha hydrogens may react in a condensation:

$$RCH_2NO_2 + R'CHO \rightarrow R'CHOHCH(NO_2)R$$

$$CH_3NO_2 + HCHO \rightarrow CH_2OHCH_2NO_2 \text{ , } (CH_2OH)_2CHNO_2 \text{ , or }$$

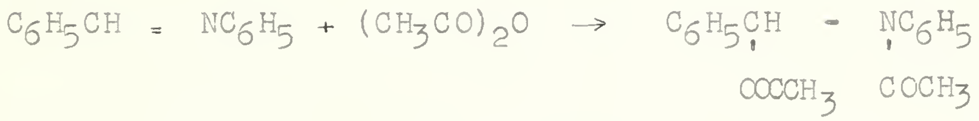
$$(CH_2OH)_3CNO_2 \text{ , depending on conditions.}$$

Azomethine compounds behave similarly to carbonyl compounds in several addition reactions (1). Mayer (2) found acetophenone to add to benzalaniline:



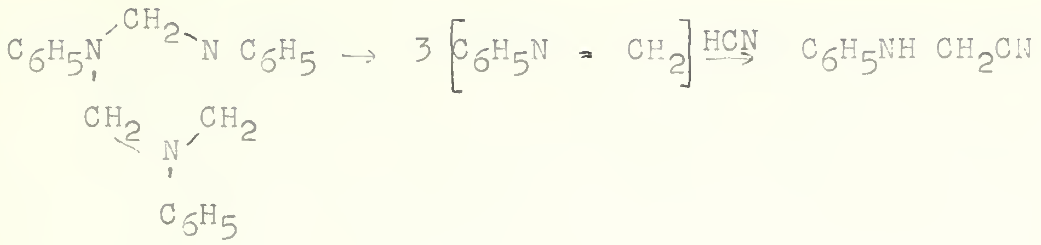
$$C_6H_5CH = NC_6H_5 + C_6H_5COCH_3 \rightarrow C_6H_5\underset{CH_2COC_6H_5}{CH} - NHC_6H_5$$

Snyder (3) reported the addition of acetic anhydride to benzalaniline:

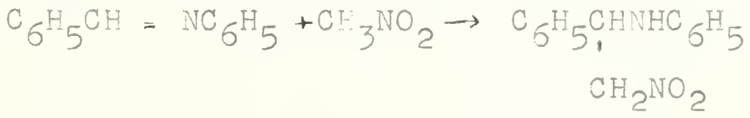


$$C_6H_5CH = NC_6H_5 + (CH_3CO)_2O \rightarrow C_6H_5\underset{OCOCH_3}{CH} - \underset{COCH_3}{N}C_6H_5$$

The addition to azomethines of such carbonyl reagents as the Grignard reagent and organo lithium compounds (4), sodium bisulfite (5), and hydrogen cyanide (6) has been reported. Miller and Plöchl (7) found that anhydroformaldehyde aniline and anhydrovaleraldehyde aniline reacted as simple monomers in the addition of hydrogen cyanide:

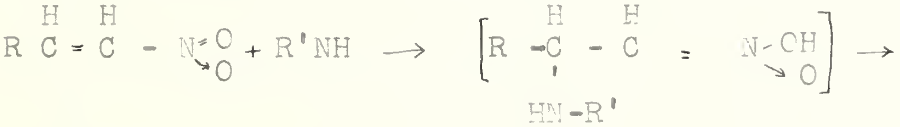


Rampine (8) found hydrogen cyanide to add to an unidentified reaction product of equimolecular amounts of aniline and butyraldehyde. In view of the similarity of the azomethine group to the carbonyl group in these addition reactions, and in view of the behavior of the nitroparaffins as carbonyl addends, nitroparaffins should add to azomethines. If the azomethine is an anil, an N-nitroalkylaniline should be obtained by this reaction. Mayer (9) does report the addition of nitromethane to benzalaniline to form N-(α-phenyl-β-nitroethyl)-aniline:

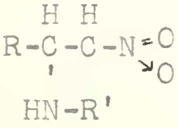


$$C_6H_5CH = NC_6H_5 + CH_3NO_2 \longrightarrow C_6H_5\underset{CH_2NO_2}{CH}NHC_6H_5$$

The synthesis of N-nitroalkyl anilines has been accomplished by the addition of amines to nitroölefines in which the unsaturation of the nitro group is conjugated with the ethylenic double bond. The reaction is postulated as taking place by an initial 1-4 addition and subsequent rearrangement of the aci-nitroparaffin.



$$R\,\overset{H}{C} = \overset{H}{C} - N\begin{smallmatrix}=O\\ \searrow O\end{smallmatrix} + R'NH \longrightarrow \left[R - \underset{HN-R'}{\overset{H}{C}} - \overset{H}{C} = N\begin{smallmatrix}-OH\\ \searrow O\end{smallmatrix}\right] \longrightarrow$$



$R-\underset{HN-R'}{\overset{H}{C}}-\overset{H}{C}-N\begin{smallmatrix}=O\\ \searrow O\end{smallmatrix}$, where R is either an aromatic or an alkyl group, and R' is an aromatic group. Wieland (10) prepared N-(β-nitroethyl)-

aniline by the addition of aniline to nitroethylene:

$$CH_2CHNO_2 \quad C_6H_5NH_2 \qquad C_6H_5NHCH_2CH_2NO_2$$

Worrall (11) prepared a series of such compounds by the addition of aromatic amines to β-nitrostyrene. Among the compounds reported are N-(α-phenyl-β-nitroethyl)-aniline, N-(α-phenyl-β-nitroethyl)-toluidine, N-(α-phenyl-β-nitroethyl)-p-aminodiphenyl, and di-N,N'-(αphenyl-β-nitroethyl)-p-phenylenediamine.

In this paper a study of the synthesis of nitroalkyl anilines by both the nitroparaffin-azomethine condensation and the addition of aromatic amines to , nitroölefines will be reported.

PREPARATION OF AZOMETHINES

Benzalaniline:

Benzalaniline was readily prepared by the method of Bigelow and Eatnough (12). Yields of 85 and 90 per cent were obtained of a product melting sharply at 51°C. (recorded melting point).

α-Ethyl-β-Propylacrolein Anil:

A modification of Snyder's (13) procedure was used in the preparation of α-ethyl-β-propylacrolein anil. One mole (126 g.) of an Eastman Kodak technical grade of α-ethyl-β-propylacrolein was placed in a four-necked flask equipped with a mercury sealed mechanical stirrer, thermometer, reflux condenser, and dropping funnel. One mole (91 cc.) of redistilled aniline was added from the dropping funnel over a period of an hour. The temperature remained at about 80°C. throughout the reaction. After the addition of the aniline, the reaction mixture was heated half an hour with a steam-bath. The cooled reaction mixture was transferred to an ordinary Claisen flask arranged for distillation under diminished pressure, and the water formed by the reaction was removed by subjection of the reaction mixture to 90 mm. pressure at 90°C. The dehydrated product was distilled under diminished pressure from a Claisen flask with an asbestos insulated, electrically heated, vigreuxed neck. A first fraction of a nearly colorless material distilled at 55-64°C. at 4-5 mm. The second fraction distilled at 128-130°C. at 2 mm., leaving a very small residue. Both fractions were analyzed for nitrogen. Fraction 1 analyzed for 3-dianilinomethyl-heptene-3, and Fraction 2 for

α-ethyl-β-propylacrolein anil.

	Found		Calculated
Fraction 1	9.44	9.40	9.52
Fraction 2	6.91	6.90	6.96

There were 18 g. of Fraction 1 corresponding to a 6.1 per cent yield of 3-dianilinomethyl-heptene 3 and 136 g. of Fraction 2 corresponding to a 67.7 per cent yield of α-ethyl-β-propylacrolein anil.

Benzalisopropylamine:

Zamschirm (14) reports the preparation of Schiff bases from benzaldehyde and aliphatic amines either by simple mixing or by mixing in alcohol solution. The Schiff base from benzaldehyde and isopropyl amine was not reported. It was desired to prepare this azomethine as the isopropylamine is readily obtainable at a reasonable price. The following procedure was adopted. One mole (101 cc.) of freshly distilled benzaldehyde was placed in a four-necked flask equipped with a mercury sealed mechanical stirrer, thermometer, reflux condenser, and dropping funnel. One mole (83.6 cc.) of Commercial Solvents Corporation isopropylamine was dropped in from the dropping funnel in about 15 minutes. The temperature rose to 70°C. during the addition of the amine. The mixture was allowed to cool to room temperature. The theoretical 18 cc. of water separated and was drawn off from a separatory funnel. The product was washed twice with 20 per cent sodium chloride solution. No trace of the strong amine odor could be

detected. The liquid was dried with anhydrous calcium chloride and distilled under reduced pressure. All of the material distilled at 115°C. at 45-48 mm. There were 117.2 g. of a nearly colorless liquid or 79.7 per cent yield of benzalisopropylamine.

Nitrogen analysis:

Found	Calculated
9.33 9.25	9.53

Butyraldehyde Anil:

Several aldehyde anils similar to butyraldehyde anil have been prepared, although the latter is not reported. Acetaldehyde anil is obtained along with ethylenedianiline by the addition of one mole of acetaldehyde to a solution of one mole in 90 per cent alcohol at 10°C. (15). Isobutyraldehyde anil was prepared by mixing one mole of aniline and one mole of isobutyraldehyde. Isobutylenedianiline was also formed in the reaction (16). Isovaleraldehyde anil is reported to be formed by the reaction of equimolecular amounts of isovaleraldehyde and aniline at 100°C. (17). Snyder (13) gives a general method for the preparation of aldehyde anils. Equimolecular amounts of the aldehyde and aniline are mixed, heated for one minute on a steam-bath, cooled to room temperature, extracted with benzene, the benzene solution dried, and the benzene removed by distillation. The product is finally distilled under reduced pressure.

(1) First preparation: The general procedure of Snyder (13) was followed in the first attempt at the synthesis of butyraldehyde

One-half mole (36 g.) of a technical grade of butyraldehyde and one-half mole (46.5 g.) of recently distilled aniline were mixed and shaken in an Erlenmeyer flask. Heat was developed. After the mixture began to cool, it was heated on the steam-bath five to ten minutes, then allowed to cool to room temperature. The mixture of yellow oil and water of reaction was extracted with 100 cc. of benzene, the benzene solution dried with anhydrous potassium carbonate, and the benzene removed by distillation. In the first attempt at distillation of the product under diminished pressure, a special distilling flask with a side arm sealed near the bulb was used. It was found that it was not possible to entirely prevent bumping over of the material from this flask. Considerable material was lost in the process. The remaining material was successfully distilled under diminished pressure from an ordinary Claisen flask. The following results were obtained:

Fraction 1 distilled at 73°-78°C. at 10 mm. - 10.0 g.

Fraction 2 distilled at 138°-159°C. at 9 mm. - 30.7 g.

Fraction 2 was redistilled, giving an additional portion of the lower boiling fraction:

Fraction 2a distilled at 80°-85°C. at 14 mm. - 10.2 g.

Fraction 2b distilled at 150°-152°C. at 9 mm. - 15.0 g.

The two low boiling fractions were combined, making a total of 20.2 g. Both low boiling and high boiling fractions were analyzed for nitrogen. The low boiling fraction gave a value corresponding to that for butylenedianiline; the high boiling for butyraldehyde anil.

	N Found		N Calculated
Fraction 1	11.27	10.75	11.66
Fraction 2	9.13	9.17	9.52

The percentage yield of butylenedianiline based on the aniline is 33.7 per cent, and of butyraldehyde anil 20.4 per cent.

(2) Second preparation: The procedure for the second preparation of butyraldehyde anil was designed to reduce the formation of the butylenedianiline. The mechanism for the formation of the desired azomethine is believed to be the initial formation of an aldehyde-aniline addition compound and subsequent elimination of water:

$$C_3H_7CHO + C_6H_5NH_2 \rightarrow C_3H_7CHOHNHC_6H_5 \rightarrow C_3H_7CH = NC_6H_5 + HOH$$

The mechanism for the formation of the alkenedianiline may be analogous to an acetal formation, the above intermediate reacting with unreacted aniline by metathetical elimination of water:

$$C_3H_7\underset{HNC_6H_5}{\overset{H}{C}}-OH + H\overset{H}{N}C_6H_5 \qquad C_3H_7\overset{H}{C}\begin{matrix}\diagup\ NHC_6H_5\\ \diagdown\ NHC_6H_5\end{matrix} + HOH$$

It was hoped that the use of an excess of butyraldehyde and cooling would facilitate conversion of all of the aniline to the postulated intermediate compound.

One mole (93 g.) of recently distilled aniline and one mole plus ten per cent excess (79.2 g.) of distilled butyraldehyde were mixed and shaken in an Erlenmeyer flask cooled in a tap water bath. The temperature of the reaction rose to 35°C. When the reaction temperature began to fall, the mixture was heated fifteen minutes

on a steam-bath and then allowed to cool to room temperature. The mixture was extracted with benzene, the benzene solution dried with anhydrous potassium carbonate, and the benzene removed by distillation. The product was distilled under diminished pressure. The following fractions were obtained:

Fraction 1 distilled at 80°-90°C. at 9 mm. - 22.0 g.

Fraction 2 distilled at 140°-159°C. at 9 mm. - 85.0 g.

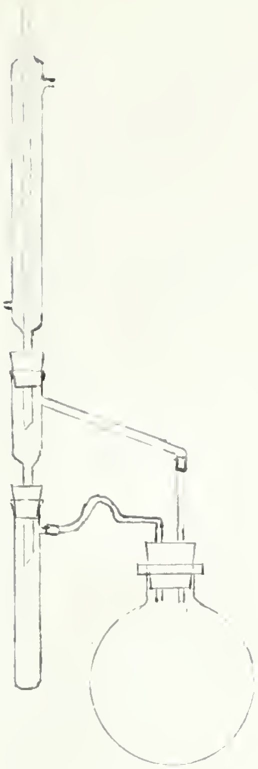
Fraction 2 was redistilled, giving an additional amount of the butylenedianiline.

Fraction 1 distilled at 80°-90°C. at 9 mm. - 31.0 g.

Fraction 2 distilled at 149°- 153°C. at 9 mm. - 48.0 g.

The total yield of butylenedianiline was 53.0 g. or 44.2 per cent based on the aniline. The yield of butyraldehyde anil is 32.6 per cent. The mole ratio of butylenedianiline to butyraldehyde anil is 1.35:1 as compared to 1.65:1 in Preparation 1.

(3) Third preparation: The reaction was carried out by mixing one mole (93 g.) of freshly distilled aniline and one mole (72 g.) of distilled butyraldehyde in 100 cc. of benzene and refluxing in the constant water separation apparatus used by Cope (18) in the preparation of ketone anils. The condensed vapors were collected in a side tube and returned to the flask by intermittent syphoning. The side tube was cooled by running tap water. The water of reaction was thus collected in the side tube.



It was hoped that the constant removal of the water formed by the reaction and the temperature of refluxing benzene solution might cause the immediate decomposition of the postulated aldehyde-aniline intermediate before reaction with aniline to form butylenedianiline might occur. Furthermore, the dilution of the reaction mixture with the solvent should decrease the possibility of the undesired reaction. After twelve hours refluxing, the theoretical 18 cc. of water of reaction had collected in the side tube. The benzene was removed from the reaction mixture by distillation, and the product distilled under reduced pressure. Only small amounts of butylenedianiline and butyraldehyde anil were obtained.

Fraction 1 distilled at 70°- 80°C. at 10 mm. - 11.7 g.

Fraction 2 distilled at 140°- 170°C. at 9 mm. - 8.0 g.

This is only a 9.7 per cent yield of butylenedianiline, and a 5.1 per cent yield of butyraldehyde anil. Most of the product was a deep red viscous material, probably a polymer of butyraldehyde

anil. The aldehyde anils do polymerize readily. However, a better conversion of reactants to the anil was achieved.

(4) Fourth preparation: To assure an infinite excess of the butyraldehyde throughout the reaction and the immediate conversion of the deficient aniline to the anil, the aniline was added dropwise to a refluxing benzene solution of the butyraldehyde. One mole (72 g.) of distilled butyraldehyde and 100 cc. of benzene were placed in a four-necked flask equipped with a mercury sealed mechanical stirrer, thermometer, reflux condenser, and dropping funnel. The solution was refluxed by heating with a steam-bath. The one mole (93 g.) of aniline was dropped in over a period of an hour and a half. Heating was continued twenty minutes after addition of all the aniline. After cooling the mixture to room temperature, the water of reaction was separated with a separatory funnel, the benzene solution dried with anhydrous potassium carbonate, and the benzene removed by distillation. The product was distilled under diminished pressure from a Claisen flask with an asbestos insulated, electrically heated, vigreuxed neck. The expected fractions were obtained.

Fraction 1 distilled at 71°-83°C. at 8 mm. - 37.3 g.

Fraction 2 distilled at 139°- 162°C. at 8 mm. - 72.0 g.

Fraction 2 redistilled:

Fraction 2a at 70°-83°C. at 8 mm. - 16.0 g.

Fraction 2b at 141°-145°C. at 8 mm. - 53.6 g.

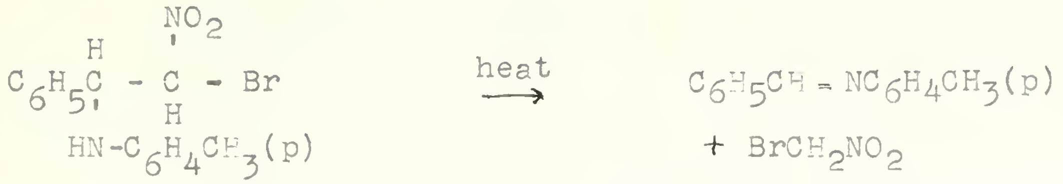
The yield of butylenedianiline is 53.3 g. or 44.2 per cent.

The yield of butyraldehyde anil is 53.6 g. or 36.5 per cent. This

yield of butylenedianiline is the same as in Preparation 2, and the yield of butyraldehyde anil is only a 3.9 higher percentage yield than in Preparation 2. Hence a simple mixing of the aldehyde and the aniline, and the maintenance of a great excess of aldehyde have given the same results.

REACTIONS OF AZOMETHINES WITH NITROPARAFFINS

That the condensation of nitroparaffins with azomethines might not proceed very readily may be suspected from the fact that the literature records rather severe conditions such as prolonged heating, and the use of active catalysts to get an aldol type of reaction with azomethines. To get an addition of nitromethane to benzalaniline, Mayer (9) refluxed the two reactants for a day. The same investigator got a condensation of acetophenone with benzalaniline by mixing equimolecular amounts of the two compounds in alcoholic solution (19). However, reaction was very slow at room temperature, about one and a half months being required. The reaction was done in an hour using an absolute methanol solution of the reactants with a sodium methoxide catalyst. Sodium methoxide was used by Kohler (20) to get condensation of nitromethane with cinnamophenone. The same condensation was carried out by Worrall (21) in a saturated solution of ammonia in 95 per cent alcohol. In the same work, Worral refers to the effectiveness of secondary amines and of sodium methoxide in promoting the condensation. The use of secondary amines as condensation catalysts is also referred to by Knoevenagel (22). Further indication that the desired addition of nitroparaffins might not go smoothly is that Worrall (23) reports bromonitromethane and benzal-p-toluidine as decomposition products from the heating of N-(α-phenyl-β-nitro-β-bromo-ethyl)-p-toluidine.



$$C_6H_5\overset{H}{\underset{HN-C_6H_4CH_3(p)}{C}} - \overset{NO_2}{\underset{H}{C}} - Br \xrightarrow{heat} C_6H_5CH=NC_6H_4CH_3(p) + BrCH_2NO_2$$

REACTION OF BUTYRALDEHYDE ANIL WITH NITROMETHANE

Experiment I:

One-quarter mole (39 g.) of freshly prepared butyraldehyde anil and one-quarter mole (15 g.) of Commercial Solvents technical nitromethane were placed in a 200 ml. round-bottomed short neck flask and refluxed for twenty hours. Bumping occurred during the reaction. A dark viscous mass formed. The material was distilled under diminished pressure. A reddish oil distilled between 142°and 152°C. at 8 mm., approximately the boiling range for butyraldehyde anil at that pressure. A black, tarry residue remained which was insoluble in acetone. The oil was analyzed for nitrogen, and a value obtained which was sufficiently near to the calculated value for butyraldehyde anil to indicate no appreciable reaction had occurred.

N Found	N Calculated
8.96 9.04	9.52

Experiment II:

A sodium ethoxide catalyst was used in this run. Two hundredths mole (.46 g.) of bright sodium metal was placed in a dry 200 ml. round-bottomed short neck flask and enough absolute ethanol added to just dissolve the resulting sodium ethoxide. Two-tenths mole (29.4 g.) of butyraldehyde anil and two-tenths mole (12.2 g.) of Commercial Solvents technical nitromethane were added. There was a precipitation of the sodium salt of nitromethane. This precipitate disappeared when the mixture was heated

to refluxing. The mixture was refluxed for four hours from a steam-bath. A dark oil resulted. Water was added to decompose the sodium ethoxide. Since the water and oil did not separate sharply, the water was saturated with potassium carbonate and the mixture was extracted with alcohol. The separated aqueous layer was extracted once more with alcohol, and the extracts combined. Most of the alcohol was removed by distillation from a steam-bath. To remove the last traces of alcohol, the material was subjected to distillation at 22 mm. from the steam-bath. The resulting product was so viscous that there was scarcely any flow at room temperature. It was attempted to distil the material under diminished pressure. Most of the material remained as a nearly solid, tarry residue. The following small fractions distilled:

Fraction 1 distilled at 80°-90°C. at 13 mm. - less than a gram
Fraction 2 distilled at 120°-160°C. at 12 mm. - 6.0 grams

Fraction 2 was redistilled with little improvement in results:

Fraction 2a distilled at 80°-100°C. at 9 mm. - less than a gram
Fraction 2b distilled at 130°-160°C. at 8 mm. - 2.7 grams

Nearly half of the Fraction 2 remained as a black tar, as a result of the redistillation. The residues were not analyzed, as it seemed unlikely that these tarry, acetone-insoluble materials which did not distil at 8 mm. pressure and 200°C., could be a product. The very small low-boiling fractions gave such qualitative tests for aniline as solubility in dilute hydrochloric acid and a primary amine test in the Hinsberg reaction for distinguishing amines. Since Fraction 2 distilled in nearly the same

range as the corresponding fraction in Experiment I, it was concluded that the material was unreacted butyraldehyde anil, as established by analysis in Experiment I.

REACTION OF BUTYRALDEHYDE ANIL WITH NITROETHANE

Experiment I:

A sodium ethoxide catalyst was used for the reaction. One hundredth mole (.23 g.) of bright sodium metal was placed in a 200 ml. round-bottomed short neck flask and just sufficient absolute ethanol added to dissolve the resulting sodium ethoxide. One-tenth mole (14.7 g.) of butyraldehyde anil and one-tenth mole (7.5 g.) of Commercial Solvents technical nitroethane were added. The sodium salt of nitroethane precipitated but disappeared on warming. The mixture was refluxed for twelve hours on a steam-bath. A dark red oil resulted. Water was added to decompose the sodium ethoxide, and the oil extracted with benzene. After the benzene solution was dried with calcium chloride, the benzene was removed by distillation. The oil was distilled under reduced pressure. Twelve and one-tenth grams of a yellow oil distilled between 140°and 156°C. at 8 mm. A tarry, acetone-insoluble residue remained.

The range at which the oil distilled indicated that it was unreacted anil. Since the N-(α-nitroethyl)-butylaniline expected for the reaction is a secondary amine, attempts were made to prepare the benzoyl and the thiourea derivatives (24). Four grams of the material was dissolved in 40 cc. of benzene, 4 cc. of benzoyl chloride added, and the mixture refluxed for an hour. The solid product which formed was recrystallized from benzene. There was less than a gram of silvery white crystals which melted at 160°-161°C. The recorded melting point for benzanilide is 160°C. A

mixed melting point proved the product to be benzanilide. To 4 g. of the oil was added 4 g. of phenylthioisocyanate. A small amount of heat was developed. In a few minutes a solid formed. Recrystallization from ligroin gave 1.2 g. of nearly colorless crystals which melted at 148.5°-149.5°C. N,N'-diphenylthiourea melts at 154°C. A mixed melting point of 149°-150°C. was obtained, indicating that this product was a slightly impure N,N'-diphenylthiourea. These same two procedures were found to give no product with pure butyraldehyde anil. Therefore, it was concluded that aniline was formed in small amounts as a result of the conditions of the experiment.

Experiment II:

An undistilled reaction product of butyraldehyde and aniline was employed as the anil in this experiment. Equimolecular amounts of aniline and butyraldehyde were mixed with cooling and left in an ice chest until water separated. The water of reaction was removed by subjection of the mixture to distillation at 22 mm. pressure from a steam-bath.

One-half gram of bright sodium metal was placed in a 500 ml. round-bottomed short neck flask and just sufficient absolute methanol added to dissolve the resulting sodium methoxide. One-half mole (73.5 g.) of butyraldehyde anil prepared as described above, and half a mole (37.5 g.) of Commercial Solvents technical nitroethane were added. A precipitate of the sodium salt of nitroethane formed which disappeared on warming. The mixture was refluxed for eighteen hours from a steam-bath. After removal

of the methanol by distillation from a steam-bath, the resulting dark red oil was shaken with 20 per cent potassium carbonate solution to decompose the sodium methoxide and to remove any remaining traces of methanol. Adhering traces of water were removed by distillation at 22 mm. from a steam-bath. The dehydrated product was distilled under reduced pressure. The following fractions were collected:

Fraction 1 distilled at 63°- 83°C. at 10 mm. - 28.6 g.

Fraction 2 distilled at 133°-173° C. at 9 mm. - 29.1 g.

Fraction 3 distilled at 198°-203°C. at 9 mm. - 25.1 g.

Fraction 1 distilled in the range for butylenedianiline which could be present as the anil used was undistilled. Fraction 2 distilled in the range for butyraldehyde anil. It was hoped that Fraction 3, which distilled somewhat higher, might be the desired N-(α-nitroethyl)-butylaniline. All three fractions were analyzed for nitrogen. Fraction 1 gave the expected value for butylenedianiline; fractions 2 and 3 both gave values corresponding to the calculated value for butyraldehyde anil:

	N. Found		N Calculated
Fraction 1	11.24	11.33	11.66 (for butylenedianiline)
Fraction 2	9.19	9.19	9.52 (for butyraldehyde anil)
Fraction 3	9.26	9.34	9.52 (for butyraldehyde anil)
			12.61 (for 1-(α-nitroethyl)-butylaniline)

Since Fraction 3 analyzed for butyraldehyde anil, but boiled somewhat higher than butyraldehyde anil, it was concluded that it

was a polymer of butyraldehyde anil. The substance is known to polymerize readily.

These attempts at the preparation of nitroalkylanilines by the addition of nitroparaffins to butyraldehyde anil gave entirely negative results. In no case was a product isolated; in all cases unreacted anil was isolated; and in all cases much of the material remained as a tarry, acetone-insoluble residue after distillation under diminished pressure. This residue is probably a polymer of unreacted anil.

REACTION OF BENZALANILINE WITH NITROETHANE

Since Mayer (9) actually reports the preparation of N-(α-phenyl-β-nitroethyl)-aniline by the addition of nitromethane to benzalaniline, it was hoped that the reaction of benzalaniline would be satisfactory even with the less reactive nitroparaffins with only two hydrogens α to the nitro group.

Experiment I:

Twenty-five thousandths of a mole (.575 g.) of bright sodium metal was placed in a dry 500 ml. round-bottomed short neck flask and 50 cc. of absolute alcohol added. After all of the sodium had reacted, a quarter of a mole (18.75 g.) of Commercial Solvents technical nitroethane was added. The bulky white precipitate of the sodium salt of nitroethane formed. Addition of 100 cc. more absolute alcohol only partially dissolved the precipitate. A quarter of a mole (45.2 g.) of benzalaniline was added, and the mixture refluxed for six hours on a steam-bath. The mixture darkened. A small amount of the precipitate remained. After removal of the alcohol by distillation, the material was treated with water to decompose the sodium ethoxide and extracted with ether. The ether was removed by distillation and the residue distilled under diminished pressure. There was no clear cut fraction for the first fraction, 15.5 g. distilling between 70°- and 140°C. at 9 mm. A second fraction distilled at 155°-165°C. at 9 mm. There were 23.0 g. of the latter. The dark residue solidified on cooling. This residue was dissolved with difficulty

in a hot mixture of alcohol and ether. After treatment with decolorizing charcoal, the solution was still very dark. On cooling, the residue separated as a viscous, tarry mass.

Fraction 1 was redistilled. A fraction of 6.8 g. distilled at 70°-72°C. at 9 mm. Four and two-tenths grams distilled at 140°-150°C. at 8 mm. The low boiling fraction was soluble in dilute hydrochloric acid, and was found to be a primary amine by the Hinsberg method. The benzenesulfonamide isolated from the latter test was recrystallized, and found to melt at 111°-112°C. Benzenesulfonanilide melts at 112°C. This was conceded to be sufficient proof that the low boiling fraction was aniline.

Two grams of Fraction 2 were treated by the Schotten-Baumann method of benzoylation. Five-tenths gram of recrystallized product was obtained which melted at 159.5°-160°C. Benzanilide melts at 160°C. In view of the boiling range and the isolation of a relatively small amount of aniline derivative, Fraction 2 was considered to be unreacted benzalaniline with traces of aniline.

Experiment II:

To 15 g. (0.2 mole) of Commercial Solvents technical nitroethane in a 500 ml. round-bottomed short neck flask was added 0.46 g. (.02 mole) of bright sodium metal. After about fifteen minutes, all of the sodium reacted to form the sodium salt of nitroethane. Thirty-six and two-tenths grams (0.2 mole) of benzalaniline was then added, and the mixture heated on the

steam-bath for fifteen hours. The precipitated sodium salt of nitroethane disappeared. The mixture was very dark. The material was treated with water and extracted with ether. After the extract was dried with calcium chloride, the ether was distilled from the extract. The product was distilled under reduced pressure. The following fractions were obtained:

Fraction 1 distilled at 68°-78°C. at 9 mm. - 7.8 g.

Fraction 2 distilled at 143°-153°C. at 8 mm. - 21.1 g.

Fraction 1 gave the same qualitative tests for aniline as the corresponding fraction in Experiment I. Proceeding on the assumption that Fraction 2 was N-(α-phenyl-β-nitropropyl)-aniline, it was attempted to reduce the material to N-(α-phenyl-β-aminopropyl)-aniline. The latter should easily give a good benzoyl derivative. Five grams of the material was dissolved in alcohol and subjected to hydrogenation at 59 pounds pressure with a Raney nickel catalyst. After two hours of this treatment, the Raney nickel was filtered off, and the alcohol removed by distillation. To assure removal of the last traces of alcohol, the material was subjected to distillation at 8 mm. from a steam-bath. The product was treated by the Schotten-Baumann method of benzoylation. Less than a gram of recrystallized material was obtained which melted at 160°C., the correct melting point for benzanilide. Evidently Fraction 2 consists of traces of aniline and another material which does not yield a benzoyl derivative in the Schotten-Baumann reaction, and which is not catalytically reduced to a compound which will give such a derivative. Fraction 2 was now analyzed

for nitrogen.

N Found		N Calculated
8.12	8.11	10.93 (for (α-phenyl-β-nitropropyl)-aniline)
		7.73 (for benzalaniline)

For comparison, some pure benzalaniline was distilled under reduced pressure and found to distil at 162°C. at 10 mm. This corresponds to the range at which Fraction 2 of both Experiments I and II distilled. In both experiments, attempts to prepare a derivative of N-substituted aniline from Fraction 2 gave small amounts of aniline derivatives. In view of these facts, and the fact that the determined percentage of nitrogen was slightly higher than that calculated for benzalaniline, it was concluded that Fraction 2 was unreacted benzalaniline with traces of aniline. The low boiling Fraction 1 was identified as aniline by qualitative tests. The heating of benzalaniline with the nitroparaffin must result in unreacted anil, some polymerization of the anil, and some decomposition with aniline as a product.

Experiment III:

For variation, the reaction was done with an inorganic alkaline catalyst, namely potassium carbonate. Two-tenths of a mole (35.2 g.) of benzalaniline, 0.2 mole (15 g.) Commercial Solvents technical nitroethane, and 1.0 g. of potassium carbonate were refluxed for five hours. Near the end of this time, bumping commenced, and what appeared to be globules of water separated. On cooling,

this material was decanted from the dark, viscous reaction mixture and found to be 2.0 g. The material was not identified. The reaction mixture was washed with water and extracted with ether. After removal of the ether by distillation, the product was distilled under diminished pressure. Most of the material remained as a black, solid residue. The material that did distil was accompanied by heavy white fumes, indicating decomposition. Results were as follows:

Fraction 1 distilled at 80°-90°C. at 8 mm. - 3.0 g.

Fraction 2 distilled at 100°C.-137°C. at 4 mm. - 7.3 g.

Fraction 3 distilled at 195°-210°C. at 4 mm. - 4.4 g.

Fraction 1, which corresponds in boiling range to Fraction 1 of Experiments I and II, was identified as aniline by the same qualitative tests that were used in these previous experiments. The benzenesulfonamide derivative melted at 110°-111°C. as compared with the recorded 112°C. for benzenesulfonanilide. Fractions 2 and 3 both consisted of a slush of solid and liquid material. The boiling range of Fraction 2 indicated that it was unreacted benzalaniline as established for the corresponding fraction in the previous experiments. It was believed that the two fractions consisted of a mixture of benzalaniline, polymeric substances of the same, traces of aniline, and traces of other possible materials formed by decomposition of the reactants. That neither fraction could be the desired N-(α-phenyl-β-nitropropyl)-aniline was indicated by the fact that neither gave a hydrogen chloride salt in Worrall's (11) procedure for forming such salts from N-nitroalkylanilines. Subsequently, it was found that such compounds

generally readily gave the salt.

Experiment IV:

All previous attempts at getting reaction between benzalaniline and nitroethane were either uncatalyzed or catalyzed by an alkaline agent. The two materials were now heated together with a trace of hydrochloric acid on a steam-bath for six hours. The mixture was distilled under diminished pressure. Practically all of the nitroethane was recovered. The residual material in the flask solidified to a dark, crystalline mass. It was recrystallized from dilute alcohol and found to melt at 51°C., the correct melting point for benzalaniline.

Experiment V:

Benzalaniline was now subjected to treatment with sodium methoxide and heating for twelve hours on a steam-bath. This was to observe the effect on benzalaniline alone of the conditions employed in Experiment I. The material, still liquid from the heating, was transferred to a Claisen flask and distilled under reduced pressure. About half the material distilled at 162°C. at 10 mm. as a yellow oil Immediately after completion of the distillation, the oil crystallized. After recrystallization from alcohol, the melting point was determined and found to be that of benzalaniline. The material remaining in the flask was a dark tarry mass similar to that resulting from the attempted reaction of benzalaniline with nitroethane.

These last two experiments show benzalaniline to be poly-

merized by heating with an alkaline agent. However, isolation of aniline and failure to get crystallization of fractions boiling at the benzalaniline range, show the introduction of nitroparaffin to have some effect.

REACTION OF BENZALANILINE WITH NITROPROPANE

To verify the results obtained for the reaction of benzalaniline with nitroethane, a similar experiment was run with the other available secondary nitroparaffin, nitropropane. Two-hundredths of a mole (.46 g.) of bright sodium metal was placed in a dry 500 ml. round-bottomed short neck flask and just sufficient absolute methanol added to dissolve the resulting sodium methoxide. Two-tenths of a mole (36.2 g.) of benzalaniline and 0.2 mole (17.8 g.) of Commercial Solvents nitropropane were added. The sodium salt of nitropropane precipitated. This precipitate partially dissolved when the mixture was warmed. After the reaction mixture was heated for twenty-four hours on a steam-bath, most of the precipitate still remained. Heating was continued forty-eight hours. Most of the precipitate had now disappeared. Water was added to decompose the sodium methoxide, the material extracted with ether, the ether solution dried with calcium chloride, and the ether removed by distillation. The product was distilled under reduced pressure. Fractions similar to those of the experiments with nitroethane were obtained.

Fraction 1 distilled at 80°-90°C. at 9 mm. - 9.7 g.

Fraction 2 distilled at 140°-156°C. at 8 mm. - 26.7 g.

Fraction 3 distilled at 200°-205°C. at 4-5 mm. - 2.3 g.

Fraction 1, which corresponded to the first fractions in the experiments with nitroethane, was tested for solubility in dilute hydrochloric acid and given the Hinsberg test for distinguishing amines. Both tests were positive for a primary amine, hence it

was concluded that the material was aniline as established in the nitroethane reaction.

Fractions 2 and 3 were analyzed for nitrogen. Both gave values indicating benzalaniline:

	N Found		N Calculated	
Fraction 1	7.96	8.06	benzalaniline.	7.73
Fraction 2	7.71	7.80	N-(α-phenyl-β-nitrobutyl)-aniline. .	10.37

This experiment thus entirely verified the results for interaction of nitroethane and benzalaniline, namely, the isolation of aniline and benzalaniline from the reaction mixture. There is no evidence of any addition of nitroparaffin to benzalaniline under the above conditions.

REACTION OF BENZALANILINE WITH NITROMETHANE

An attempt was now made to duplicate Mayer's synthesis of N-(α-phenyl-β-nitroethyl)-aniline (9). It was hoped that the failure to get addition of nitroethane and nitropropane to benzalaniline was due to the fact that these nitroparaffins are considerably less reactive than nitromethane.

Experiment I:

Two-tenths of a mole (.46 g.) of bright sodium metal was added to 100 cc. of absolute methanol in a 500 cc. round-bottomed short neck flask. Two-tenths of a mole (12 g.) of Commercial Solvents technical nitromethane was added. No precipitate of the sodium salt of nitromethane formed at this dilution. Two-tenths of a mole (36.2 g.) of benzalaniline was added, and the mixture refluxed for sixteen hours. Most of the methanol was now removed by distillation. The flask with the residual material was placed in the ice chest. After nine days, there was no evidence of crystallization. Water was now added to decompose the sodium methoxide and the material extracted with ether. The extract was dried with calcium chloride, and the ether distilled off. The product was distilled under diminished pressure. The following fractions were taken:

Fraction 1 distilled at 68°-75°C. at 8 mm. - 8.8 g.

Fraction 2 distilled at 110°-148°C. at 1-3 mm. - 4.1 g.

The Fraction 2 was not clear cut. White fumes and rapid variation of pressure of the system indicated decomposition. The residue, which represented a large part of the reaction mixture, was

black, and on cooling, solidified to a brittle, amorphous mass.

As in the reactions of benzalaniline with nitroethane and nitropropane, the low boiling fraction was shown to be aniline by qualitative tests. The benzenesulfonanilide melted at 111°-112°C. Fraction 2 was believed not to be N-(α-phenyl-β-nitroethyl)-aniline, as no hydrogen chloride salt could be obtained by the procedure of Worrall previously mentioned. The results of this experiment with nitromethane paralleled the results obtained with other nitroparaffins.

Experiment II:

In his synthesis of N-(α-phenyl-β-nitroethyl)-aniline, Mayer simply refluxed nitromethane and benzalaniline, and on cooling, obtained the crystalline product (9). An attempt was made to duplicate this work. Two-tenths of a mole of benzalaniline (36.2 g.) and 0.2 mole (12 g.) of Commercial Solvents technical nitromethane were placed in a 200 ml. round-bottomed short neck flask heated in an oil-bath. The bath was raised to 140°C., at which temperature the mixture began to reflux. After heating for twelve hours, the mixture was very dark and still refluxing. On cooling a few cubic centimeters of a watery material separated. The dark mass was nearly solid. The material was cooled in an ice chest for two hours, but no crystallization occurred. The material was then heated eighteen more hours at 140°C., making a total of thirty hours heating at this temperature. There was no change in the physical appearance of the reaction mixture.

N-(α-Phenyl-β-nitroethyl)-aniline was prepared by the method

of Worrall (11). Nitrostyrene was dissolved in alcohol and aniline added. A reddish yellow oil separated. After two hours' cooling in a freezing mixture, the oil solidified. The alcohol and product were warmed on a steam-bath until the solid dissolved and again cooled. The pure crystals formed.

Some of the crystals of pure N-(α-phenyl-β-nitroethyl)-aniline were stirred into the extremely viscous reaction product. After cooling for several hours in a freezing mixture, there was no evidence of crystallization. The material was dissolved in hot alcohol and treated with ten grams of activated carbon. There was no change in the color of the solution. On cooling, the tarry mass separated again. Further cooling in the ice chest for several days did not result in any crystallization.

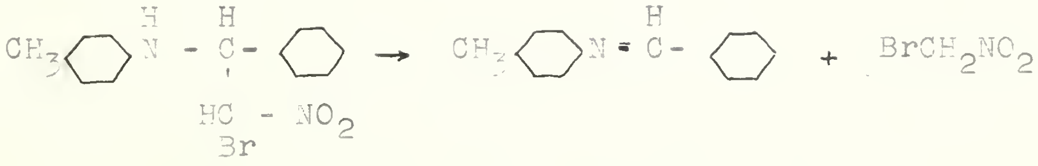
No hydrogen chloride salt could be obtained from the material by Worrall's procedure, although the known N-(α-phenyl-β-nitroethyl)-aniline readily gave the salt.

Experiment III:

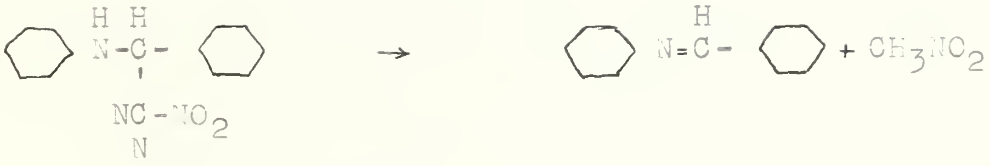
No reaction of azomethines with nitroparaffins had yet been tried with a secondary amine as a catalytic agent. Such an experiment was now tried. Two-tenths of a mole (36.2 g.) of benzalaniline, 0.2 mole (12.2 g.) Commercial Solvents technical nitromethane, and one cc. of piperidine were placed in a 200 ml. round-bottomed short neck flask heated in an oil-bath at 140°C. so that the mixture refluxed. The refluxing was prolonged for twelve hours. A reaction mixture very similar to, though somewhat less viscous

than that of Experiment I, was obtained. Cooling in a freezing mixture and seeding with crystals of pure N-(α-phenyl-β-nitroethyl)- aniline did not effect a crystallization. Worrall's hydrogen chloride salt could not be obtained.

The results of these experiments seemed to indicate that Mayer's (9) report of a synthesis of N-(α-phenyl-β-nitroethyl)-aniline by the addition of nitromethane to benzalaniline was questionable. It was recalled that Worrall reported N-(α-phenyl-β-nitro-β-bromoethyl)-p-toluidine to decompose on heating to bromonitromethane and benzal-p-toluidine (23).



Although the bromine may markedly affect the stability of this compound, it seems probable that N-(α-phenyl-β-nitroethyl)- aniline could decompose analogously to benzalaniline and nitromethane on heating.



Two-tenths of a mole (48.4 g.) of pure N-(α-phenyl-β-nitroethyl)-aniline were placed in a 125 ml. distilling flask arranged for simple distillation and heated by an oil-bath. The temperature of the oil-bath was slowly raised. When the oil bath reached 120°C., vapors appeared on the cold part of the flask. At 148°C., a few drops of material began distilling at 100°C. When the oil-

bath reached 154°C., there was vigorous frothing, and the temperature of distillation rose rapidly past 100°C. Material bumped over. After a few minutes heating at 155°C., no more material distilled. The distillate was redistilled. One and five-tenths grams of a colorless liquid distilled at 100°-101°C., 5 g. of yellow material distilled at 180°-190°C., and a solid material distilled at 290°-310°C. This solid material, after recrystallization from alcohol, melted at 87°-88°C., and was therefore identified as undecomposed nitroalkylaniline. The fraction boiling at 100°C. was found to be miscible with water, immiscible with ether, immiscible with nitromethane, and to react violently with sodium metal. This was believed to be sufficient evidence to establish the material as water. A benzoyl derivative of the fraction boiling at 180°-190°C. was found to be benzanilide. Thus, though the compound decomposed as predicted, the products of decomposition were aniline, water, and a black, tarry residue. The significant point established by this experiment was that heating pure N-(α-phenyl-β-nitroethyl)-aniline at 148°C. and heating a mixture of benzalaniline and nitromethane results in both cases in the same kind of reaction mixture, i.e., water, aniline, and a tar. From this, it seemed probable that the nitroalkylaniline was formed from the azomethine and nitroparaffin, but immediately decomposed under the conditions of reactions. Therefore, the reaction was tried under less severe conditions.

Experiment IV:

Two-tenths of a mole (36.2 g.) of benzalaniline and 0.2 mole

(12.2 g.) of nitromethane were placed in a 200 ml. round-bottomed short neck flask equipped with a reflux condenser and heated in an oil-bath. The mixture was heated for one hour at 120°C. A dark red viscous oil resulted. The oil was cooled in a freezing mixture and stirred with a few crystals of pure N-(α-phenyl-β-nitroethyl)-aniline. The sides of the flask were scratched. No crystallization occurred after standing five hours in the freezing mixture. The oil was now heated further at 120°C. After two more hours heating at 120°C., the material was dark and tarry, and the water phase had appeared. Evidently these conditions also were too severe.

Experiment V:

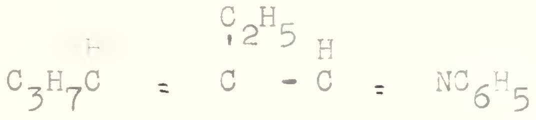
Two-tenths of a mole (36.2 g.) of benzalaniline and 0.2 mole (12 g.) of nitromethane were placed in a 200 ml. round-bottomed short neck flask equipped with a reflux condenser and heated on a steam-bath. After one hour's heating, the mixture was cooled. Benzalaniline crystallized out. After three hours' heating, benzalaniline still precipitated on cooling. After fifteen hours, the mixture was a dark oil, and no material crystallized on cooling. No crystallization was induced after five hours' cooling in a freezing mixture and intermittent scratching and stirring with seed crystals of pure product. Now 0.2 mole (12.2 g.) excess nitromethane was added, and the whole heated twelve hours on a steam-bath. The excess nitromethane was removed by distillation at 20 mm. from a 60°C. oil-bath. The residue was cooled in a freezing mixture. After four hours, crystallization occurred.

Recrystallization from alcohol gave 12.3 g. of faintly yellow crystals melting sharply at 87°C., the correct melting point of N-(α-phenyl-β-nitroethyl)-aniline. Per cent yield, 25.5 per cent.

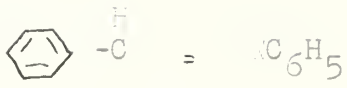
This synthesis verifies the fact that nitromethane can add to benzalaniline to give the N-(nitroalkyl)-aniline. However, the results of the other experiments show that the temperature of the reaction must be limited to that of a steam-bath to avoid complicated decomposition of the product.

REACTION OF β-PROPYL-α-ETHYLACROLEIN ANIL WITH NITROMETHANE

Benzalaniline and β-propyl-α-ethylacrolein anil are similar in having the carbon-nitrogen double bond conjugated with a carbon-carbon double bond:



$C_3H_7\overset{H}{C}=\overset{C_2H_5}{C}-\overset{H}{C}=NC_6H_5$



Although the results with benzalaniline were quite disappointing, it seemed of interest to investigate the reaction of the β-propyl-α-ethylacrolein anil with nitromethane.

Experiment I:

One-tenth mole (20.0 g.) of freshly prepared β-propyl-α-ethylacrolein anil and one-tenth mole (6.0 g.) of nitromethane were mixed and heated for 72 hours on a steam-bath. The resulting dark oil was distilled under reduced pressure. The results were very unsatisfactory. No definite fractions were recognized. Less than a cc. of a colorless liquid, possibly nitromethane, distilled at about 30°C. at 200 mm. A small amount (3.4 g.) of slightly yellow liquid was collected between 43° and 110°C. at 3 mm. A third fraction of 5.1 g. of a yellow oil was obtained between 140°-170°C. at 4 mm. During the latter part of the distillation, heavy white fumes evidenced decomposition. The large part of the reaction mixture remained as a black, brittle, acetone insoluble residue. No attempt was made at the identification of the obviously impure fractions.

Experiment II:

One-tenth mole (20.1 g.) of β-propyl-α-ethylacrolein anil,

one-tenth mole (6.0 g.) of Commercial Solvents technical nitromethane, and one cc. of piperidine were placed in a 200 ml. round-bottomed short neck flask heated in an oil-bath. The bath was maintained at 140°C. at which temperature the mixture refluxed. After heating for twelve hours, a dark viscous oil formed. It was attempted to distil the reaction product under diminished pressure. Results similar to the previous experiment were obtained. About half a gram of colorless liquid distilled at 35°-40°C. at 60 mm. Two and three-tenths grams distilled at 70°C. at 2-3 mm. This material gave a primary amine benzenesulphonyl derivative which melted at 110°-111°C., thus identifying the material as aniline. The tarry residue was difficultly soluble in hot acetone or alcohol.

Experiment III:

Subsequent to the above experiments a 25 per cent yield of N-(α-phenyl-β-nitroethyl)-aniline was actually obtained from the reaction of benzalaniline and nitromethane. Furthermore, it was established that very mild conditions must prevail for the reaction to avoid decomposition. The results of the above experiments seem to be very similar to those obtained for the benzalaniline-nitromethane reaction when the conditions were too severe. Therefore, the reaction was done under mild conditions. An excess of nitromethane was employed.

One-tenth of a mole (20 g.) of α-ethyl-β-propylacrolein anil and 0.2 mole (12.2 g.) of nitromethane were heated 15 hours in a 200 ml. round-bottomed short neck flask under reflux on a steam-

bath. The excess nitromethane was distilled off at 60°C. at 440 mm. The nitromethane distillate was cloudy, indicating some water may have been formed. The residue was distilled under diminished pressure. Two and five-tenths grams distilled at 40°C. at 3 mm. This was identified as aniline by the benzenesulphonyl derivative. The residue was dark and viscous. No further distillation was attempted. The probable formation of water, the known formation of aniline, and the tarry residue indicated decomposition had occurred. Evidently heating at the temperature of a steam-bath is too severe for this reaction.

REACTION OF BENZALISOPROPYLAMINE WITH NITROMETHANE

The azomethine of an aliphatic amine, a Schiff base, might react somewhat more readily with a nitroparaffin than the anils. Since benzalisopropylamine was readily prepared, it was used for a comparison of reactions.

Experiment I:

One-tenth mole (14.7 g.) of benzalisopropylamine and one-tenth mole (6.0 g.) of nitromethane were placed in a 200 ml. round-bottomed short neck flask and refluxed by heating with an oil-bath at 145° C. After eighteen hours' heating, the reaction mixture consisted of a small watery phase and a dark tarry phase. In this respect, the reaction mixture very closely resembled that of benzalaniline and nitromethane when heated above 100°C. The black oil was distilled under reduced pressure. A few drops distilled at 33°C. at 12 mm. Three and five-tenths grams distilled at 68°C. at 3 mm. The distillation of this fraction was accompanied by heavy white fumes. The residue was a nearly solid tar. The distillate appeared to be of indefinite composition, consisting of a mixture of yellow oil and solid. No hydrogen chloride salt could be obtained.

Experiment II:

Results nearly similar to the above were obtained using piperidine as a catalyst. Two-tenths of a mole (29.4 g.) of benzalisopropylamine, 0.2 mole (12.2 g.) of nitromethane, and a few drops of piperidine were placed in a 200 ml. round-bottomed

short neck flask equipped with a reflux condenser and heated in an oil-bath. The mixture was heated twenty-four hours at 125°C. A watery phase and a tarry phase resulted. The watery phase was decanted and found to be miscible with water. The tar was distilled under reduced pressure. Six and five-tenths grams of nearly colorless material distilled at 78°-85°C. at 12 mm. This is about the range at which benzalisopropylamine should distil. The material was insoluble in water and soluble in dilute hydrochloric acid. This was believed to be enough evidence to show the material to be unreacted benzalisopropylamine. One and five-tenths grams of a mixture of solid and liquid material distilled between 110°-160°C. at 5-6 mm. This material seemed of such indefinite composition that it was not further analyzed. The residue solidified to a black, amorphous solid on cooling.

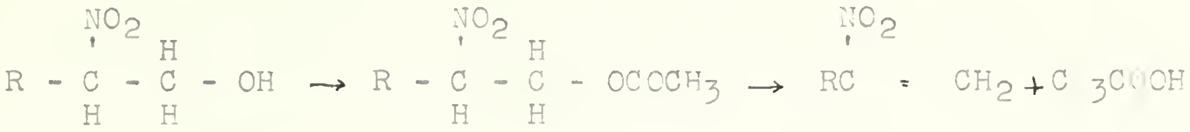
Experiment III:

The temperature of the reaction was reduced for this experiment, and an excess of nitromethane employed. Thirteen and two-tenths grams (.09 mole) of benzalisopropylamine and 11 g. (0.18 mole) nitromethane were placed in a 200 ml. round-bottomed short neck flask equipped with a reflux condenser and heated on a steam-bath. After heating for eighteen hours, there was a dark tarry material separated from the excess nitromethane. The latter was decanted off. The tarry material was transferred to an evaporating dish and exposed to the atmosphere in the hope that crystallization might occur. No crystallization was evident after twenty-four hours.

PREPARATION OF 2-NITROBUTENE-1

Nitroölefines have been prepared in low yields by the nitration of olefines with the anhydride of nitric acid at 0°C. (25) Nitroöctylene is reported to be prepared by the direct nitration of octylene with moderately concentrated nitric acid (26). Better preparations of the nitroölefines are obtained by the dehydration of nitroalcohols. The latter are easily prepared from nitroparaffins and aldehydes. The nature of the reactants or the conditions of the reaction may be such as to allow only momentary existence of the nitroalcohol as an intermediate, nitroölefine and water being isolated from the reaction (27). Several syntheses of nitroölefines by the dehydration of nitroalcohols are reported. Bouveault and Wahl (28) prepared 1-nitrohexanol-2 by the condensation of valeraldehyde and nitromethane, then dehydrated the nitroalcohol to 2-nitroöctylene-1 with anhydrous zinc chloride in glacial acetic acid solution. Cerf de Mauny (29) carried out the same reactions but used acetic anhydride heated to 120°C., as the dehydrating agent. Wieland and Sakellaris (30) obtained nitroethylene by the dehydration of β-nitroethyl alcohol with sodium bisulphate.

In this work a patented process (31) for the production of aliphatic unsaturated nitro compounds was found to give very satisfactory results. The process involves the formation of the acetyl ester of the nitroalcohol and the decomposition of the ester by heating with a trace of alkali to give the nitroolefine and acetic acid.



$$R-\overset{NO_2}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-OH \rightarrow R-\overset{NO_2}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-OCOCH_3 \rightarrow R\overset{NO_2}{C}=CH_2+CH_3COOH$$

In this laboratory (32), the following procedure for the preparation of 2-nitrobutene-1 has been adopted from the above process: One mole (119 g.) of 2-nitrobutanol-1 was placed in a three-necked flask, equipped with thermometer, dropping funnel, and reflux condenser connected to a gas-absorption trap. One mole (78.5 g., 71 cc.) plus 9 cc. excess of technical acetyl chloride was added dropwise so that the temperature was maintained at 60°-61°C. After all the acetyl chloride was added, the mixture was heated on a steam-bath until no more hydrogen chloride gas was liberated. Then the mixture was subjected to vacuum at room temperature to remove the last of the hydrogen chloride gas and the excess acetyl chloride. The material was washed twice with water and dried over anhydrous calcium chloride. The dried product was distilled under reduced pressure. A few cubic centimeters of what appeared to be water distilled at 29°-32°C. at 19 mm. This fraction was tested with potassium permanganate and found to reduce it. Since 2-nitrobutanol-1 does not reduce potassium permanganate, it was suspected that the material may contain nitroölefine. Most of the ester distilled at 108°C. at 15 mm. The yield was 134 g. or 83 per cent.

The 134 g. of ester was placed in a flask with 0.4 g. sodium hydroxide pellets and stirred. The mixture was heated to 100°C. by means of an oil-bath. At 90°C., vapors on the cold part of the flask indicated that reaction had commenced. The reaction

appeared to be somewhat exothermic as the temperature of the reaction mixture maintained about 2°C. above that of the bath. This temperature gradient held to one and three quarters to two hours, indicating reaction took place for this length of time. The reaction mixture was distilled under reduced pressure. Some distilled at 34°-35°C. at 22 mm. A good portion of the material distilled below 42°C. at 17-18 mm. Thirty-five cubic centimeters distilled at 42°-46°C. at 17 mm. This last portion was washed with saturated sodium chloride solution (water alone did not separate well) and with dilute sodium bicarbonate solution. The material was dried with calcium chloride. The dried material (42.5 g.) was distilled under diminished pressure and found to distil at 55°C. at 45 mm. The yield of 2-nitrobutene-1 was 35 g. or 34.7 per cent.

Experiment 1:

Since the decomposition of the ester appeared to commence immediately on heating to 90°C., it seemed reasonable that the reaction could be performed more rapidly and with less loss of material if the nitroölefine were distilled under diminished pressure directly from the reacting mixture. Acetic anhydride was used instead of acetyl chloride for the acetylating agent as an additional modification of the process.

A four-necked flask was equipped with thermometer, mercury sealed mechanical stirrer, dropping funnel, and reflux condenser connected with a gas absorption trap. One mole (119 g.) of 2-nitrobutanol-1 and 1 cc. of concentrated sulfuric acid were

mixed in the flask. One mole plus 5 per cent excess (107 g.) of a technical 95-96 per cent acetic anhydride was added at such a rate that the temperature of the reaction mixture remained at 55°C.±2°. Throughout most of the reaction, the mixture was a pale orange color. Very near the end, the color was a dark red. Subsequent to the addition of the acetic anhydride, the mixture was heated for an hour and a half by a steam-bath. The reaction product was washed twice with saturated salt solution and then subjected to 22 mm. pressure on a steam-bath to remove traces of acetic acid. The material was finally dried with calcium chloride.

The dried material was transferred to a 500 cc. Claisen flask equipped with a thermometer at the side arm, a thermometer in the reaction mixture, and a capillary tube. Distillation was through a short water condenser. Four-tenths of a gram of sodium hydroxide pellets was added, and the mixture heated with an oil-bath. While the temperature of the bath gradually rose, the pressure was gradually lowered. The following was observed:

Bath T.	Reaction T.	Distillation T.	Pressure	Observation
80°C.	60°C.	room temp.	606 mm.	vapors on flask neck.
105°C.	93°C.	40°C.	606 mm.	same
100°C.	95°C.	40°C.	606 mm.	exothermic reaction started
104°C.	100°C.	41°C.	610 mm.	none
103°C.	102°C.	42°C.	478 mm.	first drop in receiver
103°C.	99°C.	50°C.	200 mm.	distillation rapid
102°C.	96°C.	54°C.	200 mm.	distillation steady

Bath T.	Reaction T.	Distillation T.	Pressure	Observation
102°C.	94°C.	56°C.	200 mm.	distillation slow
100°C.	85°C.	63°C.	200 mm.	distillation very slow
103°C.	85°C.	55°C.	14 mm.	reddish material at drop per 5 sec.

About an hour was taken for this process. The distillate was a pale green. A nearly solid residue of approximately 5 g. remained in the flask. The distillate was washed three times with a solution saturated with salt and containing 5 per cent sodium bicarbonate and dried over calcium chloride. The product was distilled under diminished pressure. The material distilled at 61°C. at 42 mm. A yield of 47.5 g. or 47.0 per cent of the nitroölefine was obtained.

Experiment 2:

In the previous run, the ester was taken directly to the decomposition process without distillation and weighing. The ester was now prepared in this laboratory according to the procedure outlined in Experiment 1 (33). A 75.1 per cent yield was obtained.

The 2-nitrobutyl acetate was decomposed as described in the previous experiment, except that a lower pressure was used. The following was observed:

Bath T.	Reaction T.	Distillation T.	Pressure	Observation
110°C.	80°C.	48°C.	84 mm.	vapors condensing. equilibrium not reached
101°C.	80°C.	65°C.	84 mm.	steady distillation

Bath T.	Reaction T.	Distillation T.	Pressure	Observation
104°C.	88°C.	64°C.	70 mm.	slower distillation
105°C.	105°C.	56°C.	70 mm.	distillation ceased

About an hour was required for the reaction. A sludge was prepared of one equivalent of calcium hydroxide and sufficient water to dissolve an equivalent of calcium acetate. The distillate of acetic acid and nitroölefine was added and stirred into the sludge. Though not quite all of the calcium hydroxide dissolved, the acid was not all neutralized. Sodium bicarbonate was added until the mixture was alkaline to litmus. The layers did not separate well until the mixture was diluted with saturated salt solution. Obviously the method of separating acid and olefine was not a good one. Finally, the olefine was washed three times with saturated salt solution and dried with calcium chloride. The dried product was distilled under reduced pressure. The boiling point was 54°C. at 32 mm. The yield was 51.[illegible] g., or 51.3 per cent over-all yield based on the 2-nitrobutanol-1 or 63.3 per cent yield from the 2-nitrobutyl acetate.

A nitrogen determination gave satisfactory results for 2-nitrobutene-1.

N Found	N Calculated
13.65 13.71	13.34

REACTIONS OF AROMATIC AMINES WITH 2-NITROBUTENE-1

In contrast to the very unsatisfactory results obtained in attempts to synthesize nitroalkylanilines by addition of nitroparaffins to azomethines, the desired compounds were formed very readily with evolution of heat by the addition of aromatic amines to 2-nitrobutene-1. Satisfactory yields were obtained. The compounds were found to be comparatively easy to isolate and identify.

2-Nitrobutylaniline:

To 47.5 g. of freshly prepared 2-nitrobutene-1 were added dropwise the theoretical amount (43.7 g.) of recently distilled aniline at such a rate that the temperature was maintained at 40°C.,±2°. A reddish-orange oil resulted. No odor of the severely lachrymatory nitroölefine could be detected. A nitrogen determination of the material indicated that aniline might be in slight excess.

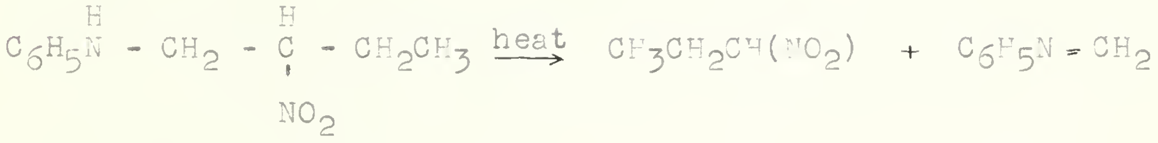
N Found		N Calculated	
14.21	14.32	2-nitrobutylaniline	14.43
		aniline	15.05
		2-nitrobutene-1	13.84

A portion (30.0 g.) was distilled under reduced pressure. A trace of material distilled before the main portion. Most of the material distilled at 65°C., at 2 mm. There were 24.8 g. in the distillate and 4.2 g. in the residue, or an 82.6 per cent yield for the reaction. The distillate and residue were analyzed

for nitrogen. The distillate gave the correct result for 2-nitrobutylaniline; the value for the residue was slightly higher.

	N Found		N Calculated for 2-nitrobutylaniline
Distillate	14.33	14.39	14.43
Residue	15.50	15.55	

An attempt was made to obtain the benzoyl derivative by the Schotten-Baumann method. Benzanilide was isolated. This may be explained by a decomposition of the 2-nitrobutylaniline by the heat and strong alkali involved in the reaction; decomposition first to give nitropropane and methyleneaniline, and then decomposition of the latter to formaldehyde and aniline.



$$C_6H_5\overset{H}{N} - CH_2 - \underset{NO_2}{\overset{H}{C}} - CH_2CH_3 \xrightarrow{heat} CH_3CH_2CH(NO_2) + C_6H_5N = CH_2$$

$$C_6H_5N = CH_2 \xrightarrow[NaOH]{HOH} HCHO + C_6H_5NH_2$$

An attempt was made to prepare the thiourea from phenylisothiocyanate, but no product was obtained. Two grams of the material was now treated by the benzoylation method of Heidelberger and Jacobs (34) In this method an acidic buffer solution of equal volumes of saturated sodium acetate and glacial acetic acid is the solvent. Three and one-tenth grams of crude product and 2.5 g. of product recrystallized from benzene were obtained. The melting point was 90.5°-91.5°C. (corrected). A nitrogen determination was made, and found correct for N-benzoyl-N-(2-nitrobutyl)-

aniline:

N Found		N Calculated
9.40	9.35	9.39

Worrall (11) found N-(α-phenyl-β-nitroethyl)-aniline and similar compounds to readily give a salt with hydrochloric acid. The material is dissolved in alcohol and concentrated hydrochloric acid added. On cooling, the salt precipitates. The salts have characteristic melting points and their identity may be established by a determination of chlorine. The 2-nitrobutylaniline readily gave this salt. It was a colorless material melting at 128.3°-129.3° C. (corrected). The salt turned red on standing several hours but could be obtained colorless by crystallization from benzene. Chlorine was determined by the Mohr method. Excellent results were obtained.

Cl Found		Cl Calculated
15.44	15.40	15.40

N-(2-Nitrobutyl)-p-Nitroaniline:

Six and nine-tenths grams of p-nitroaniline were dissolved in hot benzene and 5.0 g. (.05 mole) of freshly prepared 2-nitrobutene-1 added. The hot mixture was shaken five minutes, then cooled with tap water. A yellow solid separated as very fine needles. Recrystallization from dilute methanol gave a mat of the crystals which tenaciously retained moisture. No crystals satisfactory for a melting point determination could be obtained after drying a day

in an evacuated, concentrated sulfuric acid desiccator. The material was recrystallized from acetone without improvement. A small amount of the material was dissolved in ether, and the solution rapidly evaporated on a watch glass. The resulting film of crystals could be broken up sufficiently for the melting point determination. Melting point, 112.4°-113.4°C. (corrected). The nitrogen determination was correct for N-(2-nitrobutyl)-p-nitroaniline:

N. Found		N Calculated
17.50	17.46	17.57

The benzoyl derivative was prepared by the Heidelberger method as above. Melting point, 118.3°-119.3°C. (corrected). The nitrogen determination was correct for N-benzoyl-N-(2-nitrobutyl)-p-nitroaniline):

N Found		N Calculated
11.98	12.01	12.24

The hydrogen chloride salt was obtained, but not as readily as that of 2-nitrobutylaniline. It was a slightly yellow salt which darkened on standing. Melting point, 122.3°-123°C. (corrected). Chlorine was determined by the Mohr method and was found to be correct for N-(2-nitrobutyl)-p-nitroaniline hydrogen chloride:

Cl Found		Cl Calculated
12.85	12.79	12.88

The yield of pure N-(2-nitrobutyl)-p-nitroaniline was 5.6 g. or 46.9 per cent.

N-(2-Nitrobutyl)-α-Naphthylamine:

Seven and two-tenths grams of technical α-naphthylamine were dissolved in just sufficient alcohol to give a solution at room temperature. Five grams (.05 mole) of freshly prepared 2-nitrobutene-1 was added. Heat was developed. No solid separated, even after cooling overnight in an ice chest. The alcohol was distilled off under reduced pressure. A dark oil remained which crystallized after standing several days. Recrystallization from alcohol gave white, granular crystals. Melting point, 88.6°-89.6°C. (corrected). The nitrogen determination was correct for N-(2-nitrobutyl)-α-naphthylamine:

N Found		N Calculated
11.28	11.33	11.47

The benzoyl derivative was obtained by the Heidelberger method from the oil before crystallization had occurred. Melting point, 122.6°-123.6°C. (corrected). The nitrogen determination was correct for N-benzoyl-N-(2-nitrobutyl)-α-naphthylamine:

N Found		N Calculated
7.96	7.94	8.05

A pure white hydrogen chloride salt was obtained from the oil. Melting point, 125.5°-126.5°C. (corrected). The chlorine determination was correct for N-(2-nitrobutyl)-α-naphthylamine hydrogen

chloride:

Cl Found		Cl Calculated
12.69	12.74	12.66

The yield of pure N-(2-nitrobutyl)-α-naphthylamine was 6.4 g. or 52.5 per cent.

N-(2-Nitrobutyl)-p-Toluidine:

Five and four-tenths grams of technical p-toluidine, and 5.0 g. (.05 mole) freshly prepared 2-nitrobutene-1 were mixed in an Erlenmeyer flask. Heat was developed and an oil formed. On cooling, a yellow solid formed. Recrystallization from dilute methanol gave bright yellow flakes. Melting point, 67.5°-68.5°C. (corrected). The nitrogen determination was correct for N-(2-nitrobutyl)-p-toluidine.

N Found		N Calculated
13.36	13.30	13.46

The benzoyl derivative prepared by the Heidelberger method melted at 117.8°-118°C. (corrected). The nitrogen determination was correct for N-benzoyl-N-(2-nitrobutyl)-p-toluidine:

N Found		N Calculated
8.88	8.90	8.97

The hydrogen chloride salt was readily prepared. It was colorless and melted at 108°-109°C. (corrected). The determination of chlorine gave the correct value for N-(2-nitrobutyl)-p-toluidine

hydrogen chloride.

Cl Found		Cl Calculated
14.50	14.58	14.52

The yield of pure N-(2-nitrobutyl)-p-toluidine was 9.5 g. or 91.3 per cent.

N,N'-Di-(2-Nitrobutyl)-o-Phenylenediamine:

Four and three-tenths grams of technical o-phenylenediamine was dissolved in 20 cc. of hot water. Eight and one-tenth grams of freshly prepared 2-nitrobutene-1 were added and the mixture shaken. Heat was developed, and a reddish oil separated. After cooling twenty-four hours in an ice chest, the material solidified. Recrystallization from dilute methanol gave soft wet crystals. The material was not obtained dry after forty-eight hours in an evacuated, concentrated sulfuric acid desiccator. Recrystallization from acetone gave no improvement. After standing several days, the material recrystallized from alcohol as pale yellow needles. Melting point, 84.3°-85.3°C. (corrected). The nitrogen determination was correct for N,N'-di-(2-nitrobutyl)-o-phenylenediamine:

N Found		N Calculated
17.92	17.84	18.07

The benzoyl derivative was readily prepared by the Heidelberger method. Melting point, 123.5°-124.5°C. (corrected). The nitrogen

determination was correct for N,N'-di-benzoyl-N,N'-di-(2-nitrobutyl)-o-phenylenediamine:

N Found	N Calculated
10.67 10.69	10.81

A very bright yellow hydrogen chloride salt was obtained. Melting point, 130.6°-131.6°C. (corrected). The chlorine determination was correct for N,N'-di-(2-nitrobutyl)-o-phenylenediamine hydrogen chloride.

Cl Found	Cl Calculated
18.54 18.60	18.54

The yield of N,N'-di-(2-nitrobutyl)-o-phenylenediamine was 7.1 g. or 57.2 per cent.

determination was correct [illegible]

[illegible] ner, result [illegible]

[illegible]

[illegible]

[illegible]

[illegible]

SUMMARY

The preparation of N-nitroalkylanilines by the addition of nitroparaffins to azomethines and by the addition of aromatic amines to α-β-nitroölefines has been studied. The first method was entirely unsuccessful insofar that no new N-nitroalkylanilines were prepared. The following results were obtained:

Butyraldehyde Anil (one mole) + Nitromethane

Amt. CH_3NO_2	Catalysts	Temperature	Result
one mole	none	140°C.	Recovered anil, tar
one mole	C_2H_5ONa	100°C.	Recovered anil, tar, aniline

Butyraldehyde Anil (one mole) + Nitroethane

Amt. $C_2H_5NO_2$	Catalyst	Temperature	Result
one mole	C_2H_5ONa	100°C.	Recovered anil, tar, aniline
one mole	CH_3ONa	100°C.	Recovered anil, tar, aniline

α-Ethyl-β-Propylacrolein Anil (one mole) + Nitromethane

Amt. CH_3NO_2	Catalyst	Temperature	Result
one mole	none	100°C.	Tar, decomposition on distillation at 10 mm., aniline
one mole	piperidine	140°C.	
two moles	none	100°C.	Nearly solid tar

Benzalisopropylamine (one mole) Nitromethane

Amt. CH_3NO_2	Catalyst	Temperature	Result
one mole	none	145°C.	Nearly solid tar, decomposition on distillation at 10 mm.
one mole	piperidine	145°C.	
two moles	none	100°C.	

Benzalaniline (one mole)+Nitroethane

Amt. $C_2H_5NO_2$	Catalyst	Temperature	Result
one mole	C_2H_5ONa	100°C.	Recovered anil, tar, aniline
one mole	Na	100°C.	Recovered anil, tar, aniline
one mole	Na_2CO_3	140°C.	Recovered anil, tar, aniline
one mole	HCl	100°C.	All nitroethane recovered

Benzalaniline (one mole)+Nitropropane

Amt. $C_3H_7NO_2$	Catalyst	Temperature	Result
one mole	CH_3ONa	100°C.	Recovered anil, tar, aniline

Benzalaniline (one mole)+Nitromethane

Amt. CH_3NO_2	Catalyst	Temperature	Result
one mole	CH_3ONa	60°-100° C.	Amorphous solid, aniline
one mole	none	140°C.	Tar
one mole	piperidine	140°C.	Tar
one mole	none	120°C.	Tar, water
two moles	none	100°C.	25.5% yield of product

In all cases in which no product was obtained, most of the reaction mixture was a more or less viscous, dark tar. The more viscous tars were acetone insoluble; the less viscous ones difficultly soluble in acetone. In most cases a portion of the reacting anil was recovered and in most cases aniline was identified in the reaction mixture. A probable source of this aniline was the decomposition of the anil. Since the anils are known to poly-

merize, it was assumed that the tars might be polymerization products. Benzalaniline was found to be partly converted to such a tar after heating with an alkaline catalyst and subjection to distillation at 10 mm.

These results seemed to indicate that the azomethine group does not react as a carbonyl group in adding nitroparaffins. However, the addition of nitromethane to benzalaniline is actually reported in the literature. This reaction was finally verified, but the product of reaction was found to be highly sensitive to elevated temperatures. Indication that the product might be intermediately formed under any conditions was found in the fact that the same decomposition products were identified from a mixture of the reactants or the product of reaction when heated above 100°C. Among the products of decomposition from anhydrous materials was water. This can only be explained as a type of reduction of the NO_2 group, as this is the only source of oxygen atoms in the molecule. The exact nature of this decomposition appeared to be a problem too complex for the scope of this work.

Two facts now seem significant for the explanation of the results obtained; the fact that the anils used are subject to polymerization by the conditions used, and the fact that the expected products are subject to complex decomposition under the same conditions. It is concluded that for the experiments tried, either one or both of these courses of reaction are responsible for the failure to obtain the desired products. In general, it appears that the azomethine-nitroparaffin condensation, if such a

condensation is generally possible, can only be done under very special conditions. Indication that the reaction does not go readily is found in the fact that unreacted anil was recovered after prolonged heating with nitroparaffin. Further work may establish the specific conditions or reveal the reaction as not general.

The synthesis of the N-nitroalkylanilines by the addition of aromatic amines to nitroölefines was found very satisfactory. Though the only nitroölefine investigated was 2-nitrobutene-1; the reactions of this compound with divers aromatic amines were so satisfactory that it is believed the reaction is an entirely general one.

The nitro group and the secondary amine group in the nitroalkylanilines were found to exert considerable influence on each other as might be expected from the somewhat acidic nature of the former and basic nature of the latter. The compounds were found to be insoluble in aqueous sodium hydroxide or hydrochloric acid. The secondary amine group was found sufficiently reactive to yield to benzoylation under mild conditions, but not reactive enough to give a thiourea with phenylisothiocyanate. The hydrogen chloride salt of the secondary amine is formed by treating an alcoholic solution of the compound with concentrated hydrochloric acid.

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